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Role of Lone Pair of Electron in the Polarisation Behaviour of Aluminium in Dimethylamine

P.N.S. YADAV
Department of Chemistry
Kendriya Vidyalaya, Mughalsarai, (Chandauli)-232 101, India

The polarisation behaviour of 1100 and 3003 aluminium in aqueous solution of dimethylamine has been carried out using potentiostatic methods to explore the role of lone pair of electrons of nitrogen atom. Active-passive nature of the anodic curves has been investigated in the concentration range from 2 to 0.1% dimethylamine. By decreasing its concentration both anodic and cathodic polarisation curves have been shifted towards lower region of current density. But critical current density decreases wheras steady state corrosion potential and primary potential generally increase.

INTRODUCTION

It has been reported that nitrogen containing compounds act as corrosion inhibitors for aluminium in different corrosion media.[1–5] It has also been pointed out that their inhibitive tendency is only due to the adsorption of such molecules on metal surface. Extensive literature survey has revealed the fact that little attention has been paid to examine the effect of aqueous dimethylamine alone on aluminium surface. The present paper deals with the role of lone pair electrons belonging to nitrogen atom in the polarisation characteristics of 1100 and 3003 aluminium alloys in dimethylamine. This paper also elucidates the effect of water on polarisation behaviour.

EXPERIMENTAL

The composition of 1100 and 3003 aluminium alloys used in the present investigation (supplied by HINDALCO, Renukoot, Sonbhadra, India) was given as follows.

1100 *aluminium*: Si = 0.13%; Fe = 0.52%; Mn = 0.07%; Mg = 0.021%; Cu = 0.01% and Al = 99.25%.

3003 *aluminium*: Si = 0.16%; Fe = 0.58%; Mn = 0.78% and Al = 98.48%.

AR grade chemicals were used. All experiments were carried out in a 200 mL pyrex glass cell consisting of a flag-shaped working electrode (area 10 × 10 mm) platinum foil sealed in a glass tube as an auxiliary electrode using a Weking Laboratory model potentiostat. The preparation of elecrodes, methods of cleaning, determination of steady state corrosion potential and measurements of cathodic and anodic polarisation of 1100 and 3003 aluminium electrodes were the same as described earlier.[4] All observations were measured at 308 ± 0.2 K in air thermostat.

RESULTS AND DISCUSSION

The values of steady state corrosion potential (E_{cp}), primary passivation

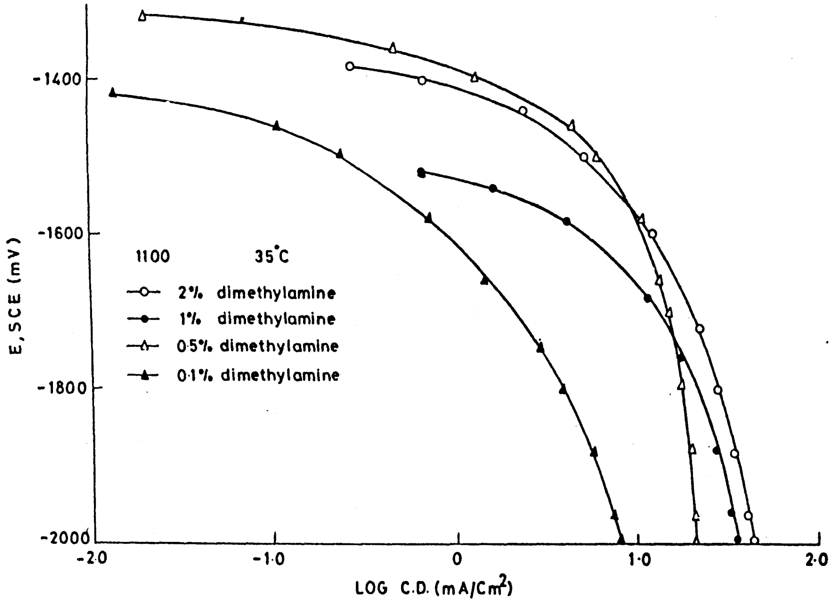

Fig. 1. Cathodic polarisation curves for 1100 aluminium electrode in different composition of

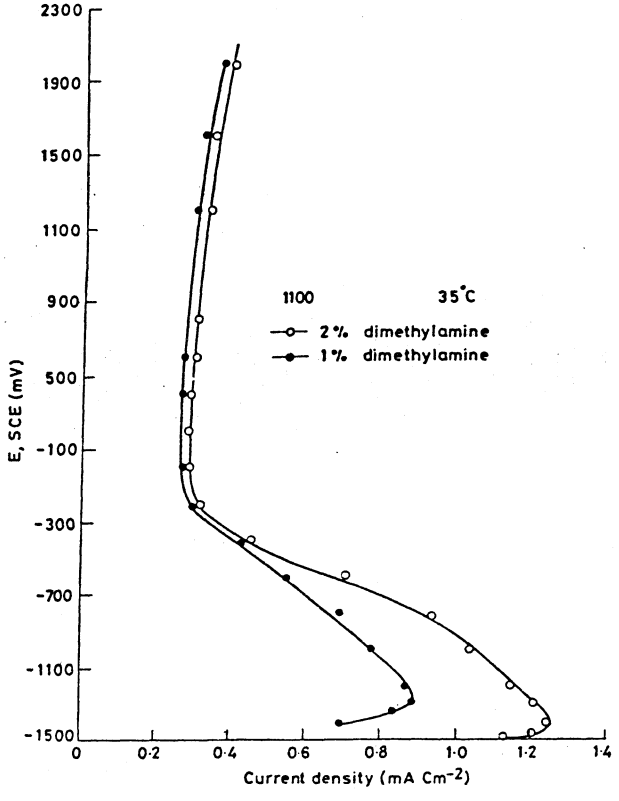

Fig. 2. Anodic polarisation curves for 1100 aluminium electrode in 2% and 1% dimethylamine.

potential (E_{pp}), breakdown potential (E_b) and critical current density (I_c) of 1100 and 3003 aluminium electrode and pH of dimethylamine after polarisation studies at 308 ± 0.2 K are given in Table-1. In general, the first two types of potentials increase while critical current density decreases with dilution of dimethylamine. It is obvious from table that the breakdown potential increases up to 0.5% concentration of dimethylamine and thereafter it decreases. Both critical current density and pH decrease as the percentage of water in dimethylamine increases.

The cathodic and anodic polarisation curves for 1100 aluminium electrode in different composition of the test solution are shown in Fig. 1 and Figs. 2–3 respectively. Curves similar to that of 1100 aluminium have been obtained for 3003 aluminium. The marked difference between the curves for the two alloys is that in case of 1100 aluminium electrode they shift more towards lower current density than the curves obtained for 3003 aluminium electrode. This is probably due to the presence of manganese, the main alloying element in 3003 aluminium, which makes the surface more electron conducting. Active-passive nature of the curves is observed in all compositions of dimethylamine. It is obvious from the figures that the degree of polarisation of the electrode increases by diluting dimethylamine.

TABLE-1

STEADY STATE CORROSION POTENTIAL (E_{cp}) PRIMARY PASSIVATION POTENTIAL (E_{pp}), BREAKDOWN POTENTIAL (E_b) AND CRITICAL CURRENT DENSITY (I_c) OF 1100 AND 3003 ALUMINIUM ELECTRODE AND pH VALUES OF DIMETHYLAMINE AFTER POLARISATION STUDIES AT 308 ± 0.2 K

Alloys and solution composition	E_{cp} (mV)	E_{pp} (mV)	E_b (mV)	I_c (mA/cm^2)	pH
1100					
2% dimethylamine	–1440	–1400	+ 400	1.250	10.36
1% dimethylamine	–1320	–1300	+ 400	0.885	10.30
0.5% dimethylamine	–1260	–1000	+ 800	0.279	10.13
0.1% dimethylamine	–1340	– 600	– 300	0.035	9.90
3003					
2% dimethylamine	–1290	–1100	+ 400	2.125	10.54
1% dimethylamine	–1160	–1160	+ 600	1.260	10.42
0.5% dimethylamine	–1070	– 900	+ 800	0.359	10.20
0.1% dimethylamine	–1100	– 500	+ 400	0.041	9.93

The active-passive nature of the corves so obtained for both alloys may be expounded on the basis of the availability of lone pair electrons of nitrogen atom and +I effect of methyl groups. Methyl group, an electron releasing group, increases electron density on the nitrogen atom. As a result, lone pair of electrons of this atom is easily available for interaction with anodic part of aluminium. Thus a film is formed on its surface. Due to this effect current density decreases with increasing potential. By virtue of the basic nature, dimethylamine exists as dimethylammonium ion in water. These ions use two hydrogen atoms linked to

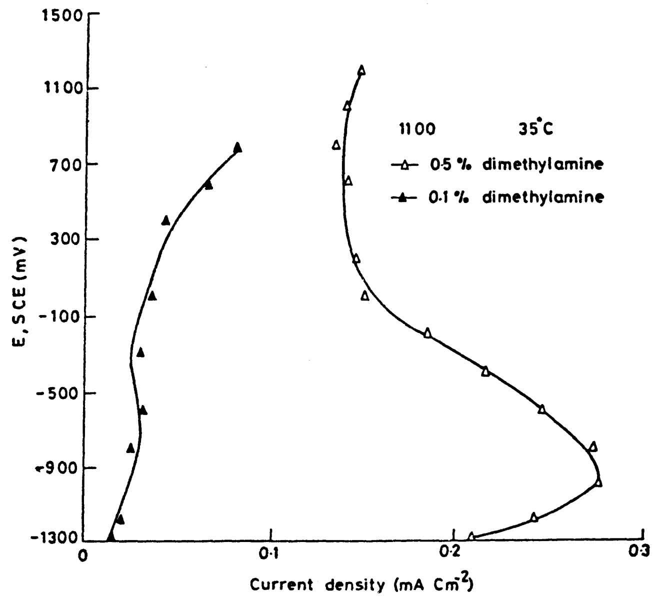

Fig. 3. Anodic polarisation curves for 1100 aluminium electrode in 0.5% and 0.1% dimethylamine.

the N-atom and form hydrogen bond with water molecules. So, they get adsorbed on the anodic sites through oxygen atoms containing lone pair of electrons during anodic polarisation of aluminium. But in case of cathodic polarisation the same ions may block the cathodic sites of aluminium by getting adsorbed *via* N-atom carrying positive charge. This is also confirmed by the fact that pH of test solution decreases after polarisation studies. Thus a greater surface area is covered. It seems that owing to this fact current density decreases in both polarisation studies by diluting dimethylamine. This explanation is further supported by the values of critical current density observed for the alloys studied.

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